

2 PRTS

09/254525

300 Rec'd PCT/PTO 08 MAR 1999

SMB

Inoc Use of Microporous Inorganic Membrane Catalysts

Consecutive and side reactions are the main cause of reduced yields and the production of chemical waste and side products in chemical production. It has now been found that undesired consecutive and side reactions can be suppressed and even completely prevented by the use of microporous membrane catalysts.

Mounting environmental restrictions and costs increasingly augment the demands on chemical production. More than 90% of the chemical products require heterogeneous catalysts in one or more steps.

A new development in research for improving chemical processes is directed to membrane catalysts. These are preferably inorganic, catalytically active membranes which have the advantage, as compared to organic membranes, of higher thermal, chemical and mechanical resistance and, in principle, unlimited capability of regeneration and sterilizability, and of being usable at higher temperatures as well. Their use improves chemical production processes through a combination of separation properties and catalytic properties. Thus, membranes can be used to change the way of performing a reaction so that the liquid or gaseous reactants separately flow over the two sides of the membrane and thus a reaction zone can form only in the interior of the membrane. The principles and characteristics of such membrane reactors known to date have been published in several review articles (J.N. Armor, Appl. Catal. 49 (1989), 1; H.P. Hsieh, Catal. Rev. Sci. Eng. 33 (1991), 1; M.P. Harold, P.

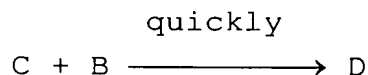
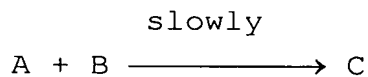
Cini, B. Patenaude und K. Venkataraman, AIChE Symp. Ser. 85 (268), 26 (1889)).

The preferential permeation of one reactant in porous membranes can be used to increase selectivity (G. Saracco, V. Specchia, Catal. Rev. Sci. Eng. 36 (1994), 305). In most cases, attempts are made to improve reaction equilibria and thus selectivities and yields by selectively separating one of the products of selectively adding one of the starting materials.

Surprisingly, in contrast to previous membrane applications, it has now been found that undesirable consecutive and side reactions in various chemical reactions can be selectively suppressed by the use of microporous membrane catalysts if the pore size of the membrane is but slightly larger than the reactants and if the reaction is performed by pressing the reaction mixture through the membrane. In the interior of the membrane, the catalytically active sites of the membrane must be preferably localized on the inner surface of the pores. Significant reactivity on the outer membrane surface adversely affects selectivity. The invention herein described is distinct from the mentioned membrane applications and others known from the literature mainly in that the membrane is not employed for permeability-selective enrichment or depletion of products, educts or catalyst poisons, but two or more mutually reacting educts are pressed together in the same direction through the catalytically active membrane. Due to the particular nanostructure of the membrane and the way of performing the reaction, the molecules are isolated in the pores and thus consecutive reactions are prevented. Thus, this membrane application for the first time allows complete separation of the product molecules from the starting materials during their generation already. This is separation in molecular dimensions which is thus distinct in principle from the activity of known larger-pore membranes.

The preparation of the coating solutions of the microporous catalyst membranes is performed according to the preparation of the mixed oxide catalysts as described in DE-A-195 45 042.6 and PCT/EP 96/00766. In all other respects, the membrane preparation is according to the methods described in US PS 5,492,873 and US 5,250,184. From those applications, it cannot be seen that a novel effective method for preventing consecutive reactions is obtained if the way of performing the reaction is changed and reactants are used which are but slightly smaller than the pores of the membrane.

The mechanism of suppressing consecutive reactions with membrane catalysts can be illustrated as follows. A reactant molecule A (e.g., hydrocarbon) reacts with a reactant B (e.g., oxygen) at the active site of the catalyst to form the desired product, molecule C (e.g., an alcohol). However, molecule C is more reactive than A (e.g., an alcohol is known to be more reactive than a hydrocarbon) and now preferably reacts with more B to quickly form consecutive products D (e.g., ketones, carboxylic acids, diols, etc., to the final products carbon dioxide and water).



This problem is known for many selective oxidation, hydrogenation and halogenation reactions and is circumvented in technology by performing the reaction with substoichiometric amounts of B with low conversions of A and short residence times. The problem is caused by the back mixing with the desired product C, which is unavoidable when the reaction is performed in the conventional way.

Such back mixing can be prevented, however, if the reaction takes place within the pores of a membrane and the pore size is not larger than twice the kinetic diameter of these molecules. Since most molecules used for heterogeneous catalysis have a size of between 0.3 and 1.5 nm, pore sizes of at least 0.6 to a maximum of 3 nm are required, depending on the molecular size. It is essential that the required pore size has a very narrow distribution and that enough catalytically active sites are present on the interior surface of such pores.

Figure 1 illustrates the effect of such pores. Above the membrane, there is the mixture/solution of the two reactants A and B. Now, the latter flow together through the pores, with the size of the pores preventing a significant change of the mixture's nature during such diffusion. If neighboring A and B molecules reach an active site during such diffusion, conversion to C may occur. If C, in the further course of diffusion until exiting from the pore, reaches other catalytically active sites, further conversion can no longer occur since there is no more B in close proximity, and additional B cannot be supplied due to the limited pore dimensions. Thus, any kinetically and thermodynamically favored consecutive reaction is prevented, and a high selectivity for the desired molecule C is achieved. This effect of prevented back mixing is clearly achievable only for the correct pore sizes of the membrane. If the pores are too large or if the pore size distribution is too broad, product selectivity is adversely affected by uncontrolled diffusion effects.

The reactor herein employed is depicted in Figure 2. The reaction can be performed correspondingly in any membrane reactor, such as tubular reactors, capillary reactors and capillary bundle reactors.

In the Examples set forth below, the selective hydrogenations, selective oxidations and selective alkylations are performed on

a wide variety of membranes, such as hydrophilic and hydrophobic, Pt- and Pd-containing, amorphous TiO_2 membranes, microporous hydrophobic V-Si-Ti mixed oxide membranes and acidic Al-Si mixed oxide membranes.

For completely suppressing back mixing, all membranes are suitable as long as they have a monomodal microporosity, active sites within the pores, and a narrow pore size distribution with pore diameters of not smaller than 0.5 nm and not larger than 3 nm. These include suitable organic membranes and defectless zeolite membranes. As the reactions the selectivity of which can be improved by the prevention of back mixing, there may be mentioned oxidation reactions, hydrogenation reactions, chlorination reactions, bromination reactions, fluorination reactions, addition reactions, cycloaddition reactions, oligomerization reactions, dimerization reactions, aromatic and aliphatic alkylation and acylation reactions, redox reactions, pericyclic reactions, substitution reactions, cyclizations, hydrolytic reactions, elimination reactions, esterifications and etherifications.

Example 1

Preparation of a hydrophobic Pt-containing catalyst membrane:

1a) Preparation of the coating solution:

In a 20 ml beaker, 0.105 g of Na_2PtCl_6 is dissolved in 10 ml of ethanol with stirring. In a 100 ml beaker, 9.5 ml of distilled titanium(IV) isopropoxide is provided under argon, and then 2.5 ml of methyltriethoxysilane (MTS) is added with stirring. Now, 40 ml of distilled ethanol (10 ml each of ethanol in intervals of 5 min) is added to the beaker. After 10 min of stirring, the following amounts of acid are successively added: 0.1 ml of 8 N HCl, after 2 min of stirring 0.1 ml of conc. HCl, after another 5 min of stirring 0.3 ml of conc. HCl, after

another 10 min of stirring 0.3 ml of conc. HCl. The Pt salt is added to the mixture with stirring, and the mixture is again diluted with 10 ml of ethanol. The mixture is subsequently stirred for several hours.

1b) Preparation of a single-coated catalyst membrane:

The catalyst is applied as a thin film to a commercially available ceramic membrane by dip coating. In this Example, a commercially available asymmetric ceramic membrane with the following characteristics was used: material: Al_2O_3 , diameter of disks: 47 mm, thickness: 2 mm, thickness of separation layer: 1.5 μm , average pore diameter: 4.5 nm. The pore sizes and pore size distributions are determined by recording the adsorption isotherm at the temperature of liquid argon or liquid nitrogen. The ceramic disks are first refluxed in a mixture of isopropanol/acetone for 4 h and subsequently dried in an oven at 400 °C for 12 h. The thus cleaned disks are coated as follows.

The ceramic disk is covered with adhesive tape on the large-pore side, attached to a thread and immersed in the above sol-gel solution 1a. In a saturated ethanol atmosphere (closed apparatus), the membrane is withdrawn from the solution with a pulling speed of 0.45 cm/min in a vibrationless way. The ceramic membrane is thereby coated with a thin gel film. After the membrane has been completely withdrawn from the solution, the thread is detached from the coupler and attached to the lid with adhesive tape. The membrane is now suspended at about 2 cm over the beaker. The latter is removed by briefly lifting the cylinder. After the beaker has been removed, 5 ml of ethanol is injected in the cylinder, and the membrane is subsequently left suspended in the alcohol atmosphere for 5 days. Thereafter, the membrane is removed and mildly calcined. In order to obtain thin films free of cracks, the membrane is dried according to the following temperature schedule: 0.1 °C/min heating rate until $T = 65^\circ\text{C}$, maintaining at $T = 65^\circ\text{C}$ for 100 min, 0.1 °C/min

heating rate until $T = 250^{\circ}\text{C}$, maintaining at $T = 250^{\circ}\text{C}$ for 300 min, cooling ($10^{\circ}\text{C}/\text{min}$) to room temperature. The remaining coating solution can be stored in a deep freezer for further coatings, or further used for the preparation of powdery catalysts.

1c) Preparation of a triple-coated catalyst membrane:

For increasing the layer thickness, the coating as described under 1b) was performed three times.

1d) Preparation of a comparative powdery Pt catalyst

The remaining coating solution from 1b or 1c was allowed to stand at room temperature for 10 h and then dried and calcined as described under 1b. The thus produced coarse glass powder is milled to the required grain size in a powder mill and employed as a powder catalyst.

Example 2

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 1b at 50°C

The single-coated membrane prepared according to the above method 1b was incorporated in a membrane reactor and activated under hydrogen flow ($10\text{ ml}/\text{min}$) at a temperature of 200°C for 12 h. Then, the temperature was decreased to the reaction temperature (50°C in this case). The reactor was filled with 10 ml of n-decane, and 200 μl of 2-hexyne was added. The mixture was then stirred for 2 min. The vessel was pressurized with hydrogen from above (hydrogen flow of $30\text{ ml}/\text{min}$ when a bubble counter was connected above the solution). The reactor was hermetically sealed. At a conversion of 22%, only 2- and 3-hexenes, but no 1-hexene and no n-hexane could be detected in the permeate (sensitivity $< 0.1\%$).

Example 3

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 1b at 110 °C

The experiment was performed as described in Example 2. At a reaction temperature of 110 °C, a conversion of more than 60% was observed in the permeate. Again, no n-hexane and no 1-hexene could be detected in the permeate, and only isomeric hexenes were formed as products.

Example 4

Selective hydrogenation of 2-hexyne in a membrane reactor with the triple-coated membrane 1c at 110 °C

The experiment was performed as described in Example 2, but using membrane 1c. In the permeate, a 2-hexyne conversion of more than 60% was achieved. Again, no n-hexane and no 1-hexene could be detected in the permeate, and only isomeric hexenes were formed as products.

Example 5

Selective hydrogenation of 1,3-hexadiene in a membrane reactor with membrane 1b at 110 °C

The single-coated membrane prepared according to the above method 1b was incorporated in a membrane reactor and activated under hydrogen flow (10 ml/min) at a temperature of 200 °C for 12 h. Then, the temperature was decreased to 90 °C. The reactor was filled with 10 ml of n-decane, and 200 µl of 1,3-hexadiene was added. The mixture was then stirred for 2 min. The vessel was pressurized with hydrogen from above (hydrogen flow of 30 ml/min when a bubble counter was connected above the solution). The reactor was hermetically sealed. At a conversion of

> 80%, only trans-2-hexene and cis-3-hexene (15:85), but no 1-hexene and no n-hexane could be detected in the permeate (sensitivity < 0.1%).

Example 6

Hydrogenation of 2-hexyne in a batch reactor

Catalyst 1d was activated under hydrogen flow at 200 °C before the reaction was begun. In 50 ml of n-decane, 0.5 ml of 2-hexyne and 100 mg of catalyst 1d (grain size < 100 µm) were stirred at 2000 rpm in a batch reactor (150 ml flask) at 90 °C under an H₂ atmosphere. The course of the reaction was followed with a gas chromatograph. Even at conversions as low as 4%, more than 70% of the product was n-hexane, 26% was 2-hexene, and 4% was trans-3-hexene.

Example 7

Hydrogenation of 1,3-hexadiene in a batch reactor

Catalyst 1d was activated under hydrogen flow at 200 °C before the reaction was begun. In 50 ml of n-decane, 0.5 ml of 1,3-hexadiene and 100 mg of catalyst 1d (grain size < 100 µm) were stirred at 2000 rpm in a batch reactor (150 ml flask) at 90 °C under an H₂ atmosphere. The course of the reaction was followed with a gas chromatograph. Here again, even at conversions of < 10%, n-hexane was the prevailing product.

Example 8

Preparation of a Pd-containing TiO₂ membrane

The preparation of the coating solution was performed according to description 1a, except that 0.035 g of Pd(II) acetylacetonate (21.5 mmol) was employed instead of Na₂PtCl₆. The prepara-

tion of the membrane was performed according to the preparation of the Pt-containing membrane described under 1b.

Example 9

Hydrogenation of 2-hexyne on Pd-containing membrane 8

The single-coated membrane prepared according to the above method 8 was incorporated in a membrane reactor and activated under hydrogen flow (10 ml/min) at a temperature of 200 °C for 12 h. Then, the temperature was decreased to 110 °C. The reactor was filled with 10 ml of n-decane, and 100 µl of 2-hexyne was added. The mixture was then stirred for 2 min. The vessel was pressurized with hydrogen from above (hydrogen flow of 30 ml/min when a bubble counter was connected above the solution). The reactor was hermetically sealed. At a conversion of 46%, only hexenes were found in the permeate. No n-hexane could be detected (sensitivity < 0.1%).

Example 10

Preparation of a catalyst membrane for acidic catalysis

a) Precoating of the membrane

A commercially available ceramic membrane with the following characteristics was used as the support membrane: diameter: 5 cm, thickness: 2 mm, pore diameter: < 1 µm. This membrane was purified according to 1b and coated twice with the following solution according to 1b: To 50 ml of ethanol was added 40 ml of TEOS, and a solution of 4 mg of ammonium fluoride in 8 ml of distilled water was added dropwise with stirring in the course of 10 min. The resulting solution was stirred at room temperature for another 2 h and then employed for double-coating the support membrane according to 1b. After firing the membrane, the following sol-gel coating solution was prepared.

b) Membrane preparation

In a 150 ml polypropylene beaker, 20 ml of TEOS (0.0783 mol) is dissolved in 25 ml of ethanol, and a solution of 4 ml of H₂O and 0.87 g of Al(NO₃)₃ (2.3 mmol) is added dropwise.

The solution is stirred for 5 min and then acidified with 500 µl of BF₃/acetate complex. With the thus obtained sol-gel solution, the precoated membrane is coated according to the dip coating method 1b. The membrane is subsequently dried under an ethanolic atmosphere for 5 days and mildly calcined. To minimize back mixing, the active aluminum-containing layer is again coated with an inactive SiO₂ layer according to 10a.

Example 11

Ethylation of biphenyl with ethanol on catalyst membrane 10

The membrane prepared by the above method 10 was incorporated in a membrane reactor and heated under argon flow (290 ml/min) at 1 °C/min to a reaction temperature of 250 °C. Biphenyl was heated at 140 °C in a separate solid evaporator and continuously evaporated and passed through the membrane with an ethylene gas flow of 10 ml/min. The permeate was cooled with dry ice, and the solids obtained were analyzed with GC. Only monoethylated biphenyls were obtained as the product.

The isomer distribution is 41% 2-ethylbiphenyl, 32% 3-ethylbiphenyl, and 27% 4-ethylbiphenyl.

Example 12

Preparation of a hydrophobic vanadium-containing catalyst membrane

The asymmetric support membrane is coated according to Example 1. For preparing the coating solution, 1.9 g of vanadium(II) acetylacetonate, 25.3 ml of TEOS, 9.7 ml of MTES, 29.0 ml of EtOH, and 7.21 ml of 8 N HCl was stirred in a PP beaker for 1 h, and the coated membrane was prepared as described under 1b.

Example 13

Selective cyclohexane oxidation on catalyst membrane 12 with TBHP

Membrane 12 was incorporated in a membrane reactor and treated by heating over night under Ar flow at 200 °C and then cooled to 90 °C. Onto the membrane, 3.04 ml of cyclohexane and 6.95 ml of TBHP (3 M solution in isooctane) was added (molar ratio of TBHP to cyclohexane = 2/1). At a conversion of 70%, only cyclohexanol and cyclohexanone at a ratio of 1:1 were present in the permeate. By increasing the flow rate, a reduction of conversion and an increase of the ratio of cyclohexanol/cyclohexanone up to 1.7 was achieved.

Example 14

Epoxidation of 1-octene with TBHP in a membrane reactor with membrane 12

The membrane reactor with inserted vanadium-containing membrane 12 was heated to 200 °C at 1 °C/min. At the same time, it was purged with argon at 90 °C. The reactor temperature was maintained for 1 h. Then, the reactor was allowed to cool to room

temperature at 0.1 °C/min under argon flow. 1-Octene (47.4 mmol, 5.32 g, 7.44 ml) and t-butylhydroperoxide (3M, anhydrous in isooctane, 9.0 mmol, 2.27 g, 3.00 ml) were successively added to the reactor. The reactor was sealed and heated to 80 °C with stirring (300 rpm). Samples were taken through the sampling valve below the membrane.

At a conversion of 11%, the permeate showed a product selectivity of > 99% for 1-epoxyoctane, the only product.

Example 15

Preparation of a hydrophilic microporous Pt-containing catalyst membrane

a) In a 20 ml beaker, 0.105 g of Na_2PtCl_6 is dissolved in 10 ml of ethanol with stirring.

In a 100 ml beaker, 12 ml of distilled titanium(IV) isopropoxide is provided under argon and stirred. Now, 40 ml of distilled ethanol (10 ml each of ethanol in intervals of 5 min) is added. After 10 min of stirring, the following amounts of acid are successively added: 0.1 ml of 8 N HCl, after 2 min of stirring 0.1 ml of conc. HCl, after another 5 min of stirring 0.3 ml of conc. HCl, after another 10 min of stirring 0.3 ml of conc. HCl. The Pt salt is added to the mixture with stirring, and the mixture is again diluted with 10 ml of ethanol. The mixture is subsequently stirred for several hours.

b) A precoated membrane as described under 10a is employed as the support membrane. The membrane preparation was performed with coating solution 16a, but otherwise as described under 1b.

Example 16

Selective hydrogenation of 2-hexyne in a membrane reactor with membrane 16 at 60 °C

2-Hexyne was reacted on the membrane as described under 2 at a reaction temperature of 60 °C. At a conversion of 10%, cis-2-hexene could be detected in the permeate as the only product.